

# Fly-Ash Particles and Precipitated Silica as Fillers in Rubbers. II. Effects of Silica Content and Si69-Treatment in Natural Rubber/Styrene–Butadiene Rubber Vulcanizates

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**ABSTRACT:** This article explored the possibility of using silica from fly-ash particles as reinforcement in natural rubber/styrene–butadiene rubber (NR/SBR) vulcanizates. For a given silica content, the NR : SBR blend ratio of 1 : 1 (or 50 : 50 phr) exhibited the optimum mechanical properties for fly-ash filled NR/SBR blend system. When using untreated silica from fly-ash, the cure time and mechanical properties of the NR/SBR vulcanizates decreased with increasing silica content. The improvement of the mechanical properties was achieved by addition of Si69, the recommended dosage being 2.0 wt % of silica content. The optimum tensile strength of the silica filled NR/SBR vulcanizates was peaked at 10–20 phr silica contents. Most mechanical properties increased with thermal ageing. The addition of silica

from fly-ash in the NR/SBR vulcanizates was found to improve the elastic behavior, including compression set and resilience, as compared with that of commercial precipitated silica. Taking mechanical properties into account, the recommended dosage for the silica (FASi) content was 20 phr. For more effective reinforcement, the silica from fly-ash particles had to be chemically treated with 2.0 wt % Si69. It was convincing that silica from fly-ash particles could be used to replace commercial silica as reinforcement in NR/SBR vulcanizates for cost-saving and environment benefits. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3396–3405, 2007

**Key words:** rubber; reinforcement; mechanical properties; silica; vulcanization

## INTRODUCTION

A rubber compound must be reinforced mainly with carbon black and silica to improve the end-product performances, and it is generally accepted that the reinforcing phenomenon in the filled rubber compound is, to a large extent, dependent on the physical interactions between the filler and rubber matrix, which are related to the active functional groups of the filler surfaces. This also determines the degree of adhesion at interfaces, which reflect the properties of the rubber products. Recently, synthetic-precipitated silica has been widely used in rubber reinforcement and has proved to be as effective as carbon black.<sup>1</sup> Extensive works in the silica/rubber system are focused on the interactions between silica particles and rubber molecules. Silica surfaces have hydrophilic siloxane and silanol groups, resulting in strong

filler–filler interaction by hydrogen bonds.<sup>2</sup> The silanol groups are acidic and can interact with the basic accelerators causing long cure time and slow cure rates. As a result, dispersing silica in rubber compounds is much more difficult than carbon black dispersion. Silane coupling agents, such as bis (3-triethoxysilylpropyl) tetrasulfide (TESPT) and bis (3-triethoxysilylpropyl) disulfide (TESPD) are used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface. Silica can be found in various sources, such as precipitated silica by precipitation of an aqueous sodium silicate solution, fumed silica by pyrogenic process, and silica from natural resources (e.g., rice husk ash and fly-ash). In recent years, silica from natural resources have attracted rubber technologists as an alternative reinforcing filler in natural and synthetic rubber compounds because of cost-saving, good mechanical properties, better dimensional stability, and environmental issues.

In thermal power plant stations, fly-ash particles are carried out of the boiler by flue gases and extracted by electrostatic precipitators and filter bags. As a general problem, the ash particles generated at thermal power plant need to be disposed outside the plant premises.<sup>3</sup> The disposal of fly-ash

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is becoming more expensive each year because of large land needed for its disposal. The best way to solve the disposal problem of fly-ash is to make productive use of fly-ash particles, one of which being to utilize the fly-ash as a filler in polymeric materials. This is possible since the fly-ash contains nearly 40–50% silica by weight of the total fly-ash and the price is relatively low ( $\sim 50$  times cheaper than any commercial silica, based on the purchasing price in Thailand).<sup>4,5</sup>

Experimental data and information on the use of fly-ash particles as a potential filler in rubber materials have been very rare. Only a few works<sup>6,7</sup> have investigated the effects of fly-ash particles on the properties of rubber vulcanizates. Garde et al.<sup>6</sup> suggested that the mechanical properties of polyisoprene rubber loaded with fly-ash particles were inferior to that filled by silica, but the property improvement for the fly-ash filled rubber vulcanizates could be obtained by incorporating an appropriate amount of silane coupling agent into the compounds.<sup>7</sup> Mishra et al.<sup>8</sup> showed that the  $\text{CaCO}_3$  nanoparticles performed a better reinforcing effect on improving the mechanical strength and flame retardancy than the FA particles in the polybutadiene rubber, the reasons being associated with more uniformity in dispersion of nanoparticles in the rubber matrix; similar findings were reported by Hundiwale et al.<sup>9</sup> Sombatsompop et al.<sup>4</sup> introduced untreated FA particles into NR vulcanizates and found that the mechanical properties of FA-filled NR vulcanizates appeared to be very similar to those of commercial silica-filled vulcanizates at silica contents of 0–30 phr. Above these concentrations, the properties of the FA-filled compounds remained unchanged, the FA particles being used as an extender. The properties of the FA-filled NR compounds were found to improve with the addition of bis(3-triethoxysilylpropyl) tetrasulfane (Si69) coupling agent at 2.0–4.0 wt %.<sup>5</sup>

The findings in this work were proposed since it has been recently found that experimental data on the use of fly-ash particles as potential filler in any rubber blend systems are not available. This proposed work especially continued from our previous work published in *Journal of Applied Polymer Science*,<sup>4</sup> and currently aimed to seek the optimum blend ratio of NR and SBR and to study the effects of Si69-treated fly-ash contents on the properties of the NR/SBR blends. A wide range of the properties of the fly-ash filled rubber compounds were studied, including cure time, crosslink density, tensile modulus, tensile and tear strengths, hardness, abrasive resistance, compression set, and resilience. The effect of thermal ageing was also of interest. The results were compared with those of NR/SBR blend filled with commercially available silica.

## EXPERIMENTAL

### Rubber and fillers

Natural rubber (NR, STR20), supplied by Huay Chuan (Bangkok, Thailand), and styrene-butadiene rubber (SBR, SBR1712), supplied by BST Elastomers (Bangkok, Thailand) were used in this work. The SBR comprised of 24.5% styrene, 28.8% oil, and 5.7% organic acid.

Commercial precipitated silica (designated as PSi) and silica from fly-ash particles (designated as FASi) were used as potential fillers for this study. The fly-ash (FA) particles were supplied by Mae Moh Power Station of KNR Group (Lampang, Thailand). The characteristics (dimensions and shape) of the fly-ash particles can be found in our previous work.<sup>4</sup> The FA particles used in this work were made of round-shaped particles with relatively smooth surfaces, and had an average particle size and pH of 50–100  $\mu\text{m}$  and 9.5, respectively. The commercial precipitated silica was a Tokusil 233, supplied by the Tokuyama Siam Silica (Bangkok, Thailand), having an average particle size of 50–100  $\mu\text{m}$ , a pH of 6.8, a bulk density of 0.232  $\text{g cm}^{-3}$ , and a BET surface area of 128  $\text{m}^2 \text{g}^{-1}$ . According to our previous results on chemical composition of the fly-ash particles in comparison with commercial grade silica, the major component of FA was  $\text{SiO}_2$  ( $\sim 46.25\%$ ).<sup>4</sup> Both fly-ash and commercial silica had the same functional groups (e.g., silanol and siloxane groups at wave-numbers of around 3400 and 1100  $\text{cm}^{-1}$ , respectively).<sup>5</sup> This work intended to investigate the effect of chemical surface treatment on fly-ash particles on the cure and mechanical properties of NR/SBR vulcanizates with various silica (in fly-ash) contents, and to compare the reinforcing effectiveness with the PSi filled NR/SBR vulcanizates at specified silica content. It should be noted that the required silica (FASi) content in the fly-ash particles added to the rubber compounds had to be calculated based on the fact that there was 46.25% silica in fly-ash particles.

### Filler surface treatment by Si69

Bis-(3-triethoxysilylpropyl) tetrasulfane (designated as Si69),  $[(\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_3\text{S}_4-(\text{CH}_2)_3\text{Si}-(\text{C}_2\text{H}_5\text{O})_3]$ , was used as a chemical coupling agent, supplied by JJ-Degussa (Bangkok, Thailand). In this work, the Si69 at various concentrations were utilized for surface treatments of the FASi and PSi fillers. The surface treatment procedure commenced by mixing 2.0 g of Si69 with 100 mL of ethanol, and then stirred for 30 min. Around 100 g of FASi or PSi was then added into the solution with a further 15 min stirring to ensure a uniform distribution of the coupling agent on the FASi and PSi surfaces. The treated FASi and PSi were then dried at 100°C for 12 h in an oven until a constant weight was achieved.<sup>5</sup>

**TABLE I**  
**Vulcanizing Recipe for NR/SBR Blend Compounds**

Ingredients	Content (phr)
1. NR/SBR (at various blend ratios)	100
2. ZnO	5.0
3. Stearic acid	3.0
4. MBT (mercaptobenzthiazol)	0.3
5. Antioxidant butylated hydroxytoluene	1.0
6. Sulfur	1.5
7. Polyethylene glycol (PEG)	5.0
8. Filler (fly ash and commercial silica grade)	Varying from 0–50

### Rubber blending and sample preparation

#### Mastication and compounding

The formulation of the rubber blend compounds, in parts per hundred rubber (phr), is shown in Table I. The blend ratio of NR to SBR varied from 100 : 0, 25 : 75, 50 : 50, and 75 : 25 to 0 : 100. There were two steps for making the rubber blend products (samples) for property evaluations, these being mastication and compounding processes. In the mastication step, the two rubbers were masticated and blended on a laboratory two-roll mill (Yong Fong Machinery, Samutsakon, Thailand) for 5 min, followed by mixing with a specified content of fillers (silica or fly-ash) for a further 20 min. On entering the compounding step, the rubber blend and filler were compounded with prepared vulcanization chemicals on the two-roll mill for a further 20 min, the compound being then kept at 25°C with 50% humidity prior to further use.

#### Vulcanization of NR/SBR blends

The resultant rubber compound was then compression-molded to a 90% cure using an hydraulic press (LAB TECH, Bangkok, Thailand) at 170 kg cm<sup>-2</sup>, using 160°C cure temperature to give vulcanized rubber.

### Vulcanizates characterizations

#### Cure time determination

The cure time used for any individual compound was predetermined by an Oscillating Disk Rheometer (Model ODR GT 7070-S2), GOTECH Testing Machine, Taiwan) using ASTM D2084-01 at a test temperature of 160°C.

#### Physical and mechanical properties

- Crosslink density: The determination of the crosslink density of the vulcanized rubber blends was carried out using a swelling method.<sup>10</sup> The experi-

mental procedure commenced when the vulcanized rubber blend samples were cut into small pieces (2 × 2 cm<sup>2</sup>) and then weighed before being immersed in toluene. The samples were kept in a dark place for 7 days. Excess liquid on the surface of the specimens was removed by blotting with filter paper. The swollen samples were taken out and placed for drying at a controlled temperature of 21°C. The weight of the swollen samples was measured, and the crosslink density was calculated using the Flory-Rehner equation as shown below, the details of the calculations being found elsewhere.<sup>4</sup>

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = 2V_s \eta_{\text{swell}} \left( V_r^{1/3} - \frac{2V_r}{f} \right) \quad (1)$$

where  $V_r$  is the volume fraction of rubber in swollen gel,  $V_s$  is the molar volume of the toluene (in this work being 106.2 cm<sup>3</sup> mol<sup>-1</sup>),  $\chi$  is the rubber-solvent interaction parameter (in this case being 0.3795 for NR and 0.413 for SBR). In the case of NR/SBR blend system, the  $\chi$  value used varied according to the ratio of each rubber.  $\eta_{\text{swell}}$  is the crosslink density of the rubber (mole/cm<sup>3</sup>),  $f$  is the functionality of the crosslinks (being 4 for sulfur curing system).

- The tensile properties (modulus at 200% elongation, tensile strength, and elongation at break) of the rubber vulcanizates were tested according to ASTM D412-98 (1998) with use of dumbbell-shaped samples, the tests being carried out using the universal testing machine Model Autograph AG-I, Shimadzu (Tokyo Japan).
- Tear strength was determined according to ASTM D624-00 (2000) using angle-shaped samples and a Shimadzu tear strength testing machine. Both tensile and tear properties used a testing speed of 500 mm/min.
- A hardness durometer (Shore A) Model 475, PTC instruments, (MA) was used for hardness tests, the test conditions being in accordance with ASTM D 2240-03 (2003).
- Resilience property was, according to ASTM D2632-01(2001), performed on a Wallance Dunlop Tripsometer (H.W. Wallance and, Kingston, UK).
- The abrasive resistance was evaluated using a standard test according to DIN 53,516, performed on a DIN abrader (Hampden Test Equipment, Northants, UK).
- Compression set was assessed using ASTM D395-01 (2001) at a test temperature of 100°C for 22 h.

#### Thermal ageing

The effect of thermal ageing on the property changes of the NR/SBR blend filled with Si69 treated FASI

**TABLE II**  
Cure Time and Mechanical Properties of NR : SBR Blend with 20 phr FASi

NR : SBR blend ratio (phr)	Properties of NR : SBR with 20 phr FASi					
	Cure time (min)	Modulus at 200% ( $\times 10^5$ Pa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)	Hardness (Shore A)
0 : 100	31	2.2 $\pm$ 0.1	1.2 $\pm$ 0.1	720 $\pm$ 10	6.8 $\pm$ 0.3	34 $\pm$ 1
25 : 75 (1 : 3)	21	2.7 $\pm$ 0.1	2.6 $\pm$ 0.2	1016 $\pm$ 15	8.2 $\pm$ 0.4	38 $\pm$ 0
50 : 50 (1 : 1)	16	3.1 $\pm$ 0.1	4.3 $\pm$ 0.3	1126 $\pm$ 26	10.0 $\pm$ 0.4	36 $\pm$ 0
75 : 25 (3 : 1)	15	3.0 $\pm$ 0.2	5.0 $\pm$ 0.6	1096 $\pm$ 20	9.7 $\pm$ 0.2	35 $\pm$ 1
100 : 0	12	2.2 $\pm$ 0.1	4.5 $\pm$ 0.1	900 $\pm$ 12	9.3 $\pm$ 0.5	27 $\pm$ 1

filler was studied using a standard method of ASTM D573-99 (1999). The silica filled vulcanizates were aged at an oven temperature of 70°C for 96 h and then left at room temperature for 16 h before testing. The mechanical properties of the vulcanizates before and after thermal ageing were then evaluated.

#### SEM studies

Failure mechanisms were investigated using a JEOL (JSM-6301F) SEM machine at 15 kV accelerating voltage. The fracture surfaces for examination were obtained from tensile-fracture surfaces. The experimental procedure can be obtained elsewhere.<sup>11</sup>

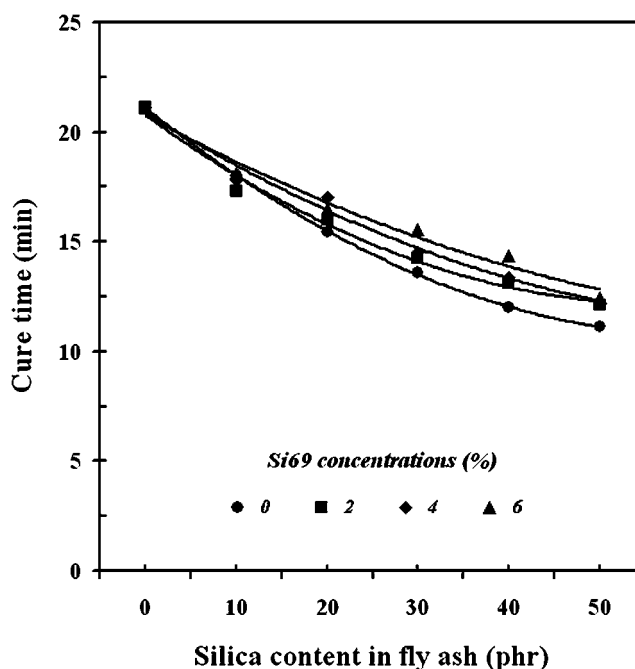
## RESULTS AND DISCUSSION

#### Effect of NR/SBR blend ratio

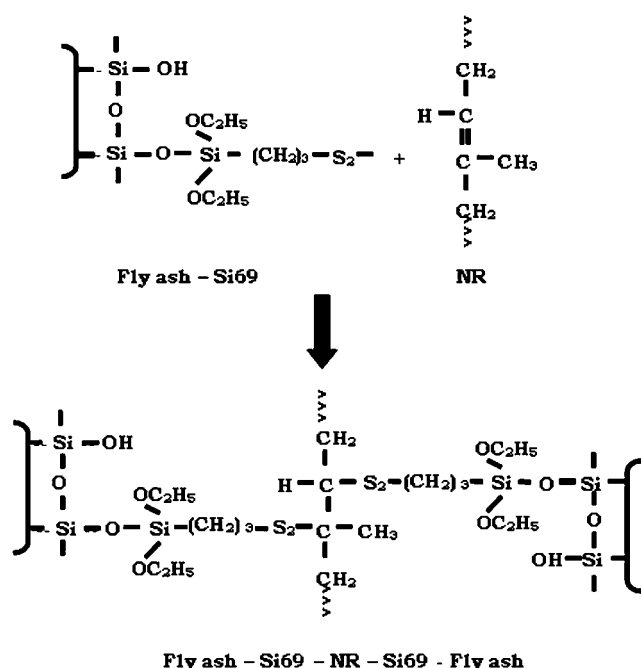
The first part of this work was to seek a suitable NR/SBR blend ratio for optimum cure and mechanical properties of the fly-ash filled NR/SBR vulcanizates. Table II shows the effect of NR/SBR blend ratio on the cure and mechanical properties for NR/SBR vulcanizates containing 20 phr silica from fly-ash. It can be seen that the cure time decreased with increasing NR content, the neat NR requiring shorter cure time to vulcanize than the neat SBR. This could be explained by three possible reasons; (i) NR has more reactive sites to form crosslinks during vulcanization than SBR, (ii) molecular structure of NR is simpler and more flexible than that of SBR, this making the crosslinking process of NR more feasible, and (iii) SBR has a benzene group in the molecule, which could result in a steric effect to the crosslinking reaction. In the case of mechanical properties of the NR/SBR vulcanizates, it was found that the overall mechanical properties progressively increased up to the NR:SBR blend ratio of 1 : 1 (or 50 : 50 phr), and then decreased when increasing NR content. It was interesting to note that the mechanical properties of the FASi/NR/SBR vulcanizate at 1 : 1 (50 : 50 phr) blend ratio were greater than those for the neat FASi/NR or neat FASi/SBR vulcanizate.

#### Effects of FASi and Si69 concentrations and thermal ageing

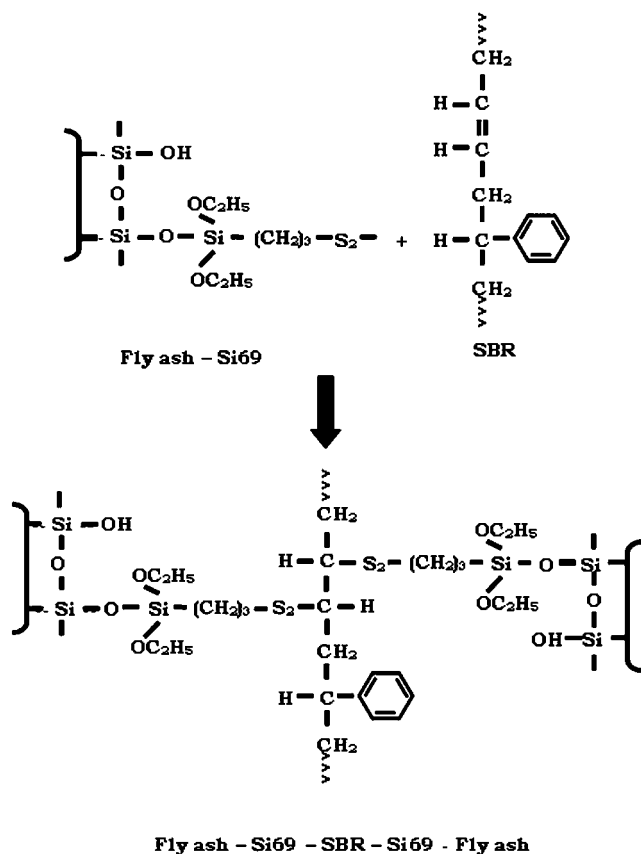
This part selected the NR/SBR compound at a blend ratio of 1 : 1 (50 : 50 phr) for studying the effects of FASi content and surface treatment by Si69. Figure 1 shows the effect of silica (FASi) loading on the cure time for NR/SBR vulcanizates varying Si69 contents. It was found that FASi had an effect on the cure time change, the cure time progressively decreasing with silica loading. This was because the NR/SBR vulcanizates with FASi had excessive metal oxides (such as Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO) present in the fly-ash particles, and these metal oxides acted as activators, and thus accelerated the vulcanizing process.<sup>4,5</sup> This has a practical benefit for the rubber manufacturer in terms of production time minimization. For the Si69 treatment effect, it can be observed that the addition of Si69 had a reverse effect on the cure time as compared with that of FASi, the cure time slightly increasing with Si69 content. The increase in cure



**Figure 1** Effect of FASi content on cure time using different Si69 concentrations for 50 : 50 NR/SBR vulcanizates.



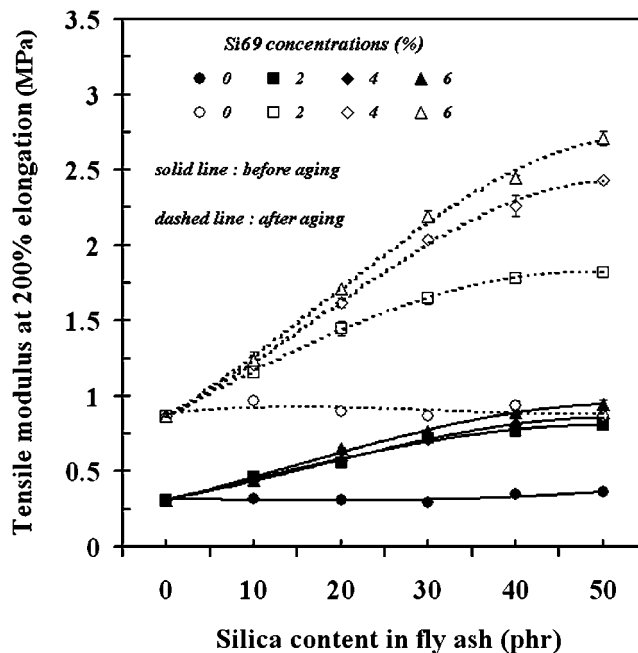
**Scheme 1** A chemically coupling reaction of silica in fly-ash and NR via Si69.



**Scheme 2** A chemically coupling reaction of silica fly-ash and SBR via Si69.

time indicated an interference effect on the crosslink formation of the rubber caused by the presence of Si69. This can be explained using chemical reactions between Si69-treated fly-ash particles and the being-vulcanized rubbers as shown in Scheme 1 for FASi-Si69-NR system and in Scheme 2 for FASi-Si69-SBR system. It can be seen that the reactive radicals on the rubber occurring during the mastication process may have to form a chemical C—S linkage with the Si69.<sup>12,13</sup> This would automatically reduce chances to form S—S crosslinks within the rubber molecules themselves. Another reason could be due to the formation of longer chains of Si69, which consist of triethoxysilylpropyl groups on their molecules. These bulky triethoxysilylpropyl groups probably caused a steric hindrance for rubber crosslinking. This explained why the cure time was prolonged by increasing Si69 content, this view being supported by Poh and Ng.<sup>14</sup>

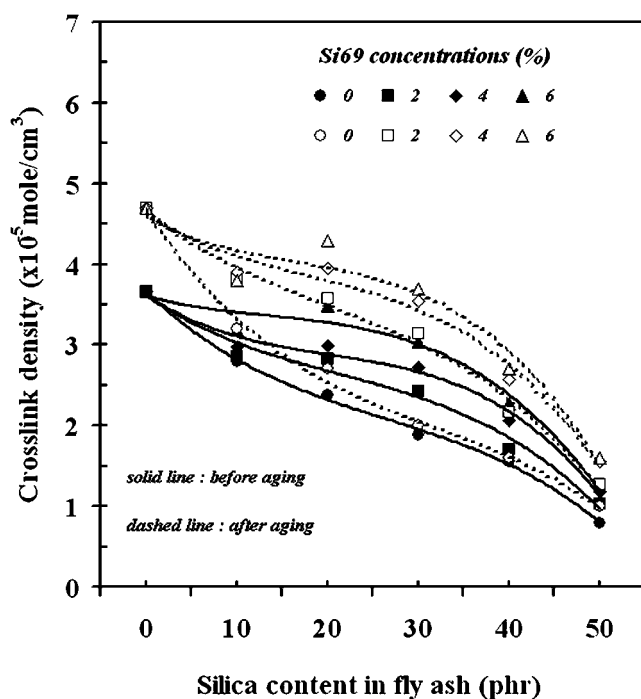
Figure 2 shows the tensile modulus at 200% elongation for NR/SBR blend (NR/SBR blend ratio of 1 : 1 or 50 : 50 phr) vulcanizates containing different concentrations of FASi and Si69 before and after thermal ageing conditions. Before thermal ageing, it was found that addition of FASi had no effect on the tensile modulus for the untreated FASi/NR/SBR vulcanizates, but resulted in a progressive increase in the tensile modulus with addition of 2.0 wt % Si69 treated FASi, the latter being due to rigidity change of the rubber blend as a result of adding fly-ash particle. Higher Si69 contents (4.0–6.0 wt % Si69) did not affect the tensile modulus of the vulcanizates. It can be seen that the overall tensile modulus



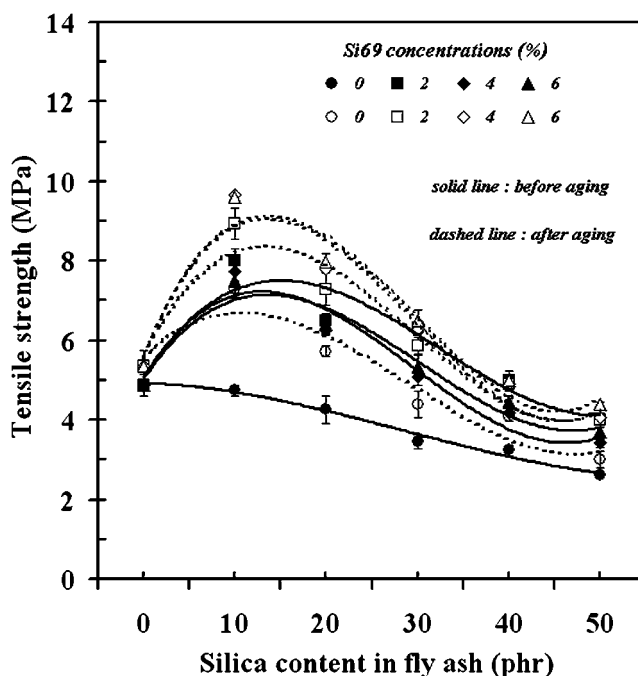
**Figure 2** Changes in tensile modulus at 200% elongation as a function of silica and Si69 contents for 50 : 50 NR/SBR vulcanizates.

significantly increased after thermal ageing. This was due to a postcuring effect, which has produced more crosslinks in the vulcanizates. The increase in crosslinks can be confirmed by considering Figure 3 illustrating the changes in crosslink density for Si69-treated FASi/NR/SBR vulcanizates with various FASi and Si69 contents. As can be observed, the crosslink density of the vulcanizates shifted after thermal ageing. The crosslink density of the vulcanizates decreased with increasing FASi content, but increased with increasing Si69 loading. The decrease in crosslink density with the presence of FASi particles may be caused by an interference effect from added fly-ash particles to the crosslinking reaction, while the increase in crosslink density was due to the Si69 which had produced additional crosslinks as a result of C—S linkages formed between the rubber and the Si69 molecules (Schemes 1 and 2). This implied that Si69 could act as a secondary crosslinking agent in the NR/SBR vulcanizates.

Figure 4 shows the tensile strength for NR/SBR vulcanizates with varying FASi and Si69 contents before and after thermal ageing conditions. Before thermal ageing, the vulcanizates filled with untreated FASi showed a progressive decrease in tensile strength with increasing FASi content as expected, because of low filler–rubber interactions.<sup>15</sup> The tensile strength of the Si69-treated FASi/NR/SBR vulcanizates increased at the FASi contents of 10–20 phr, and then decreased at higher FASi load-



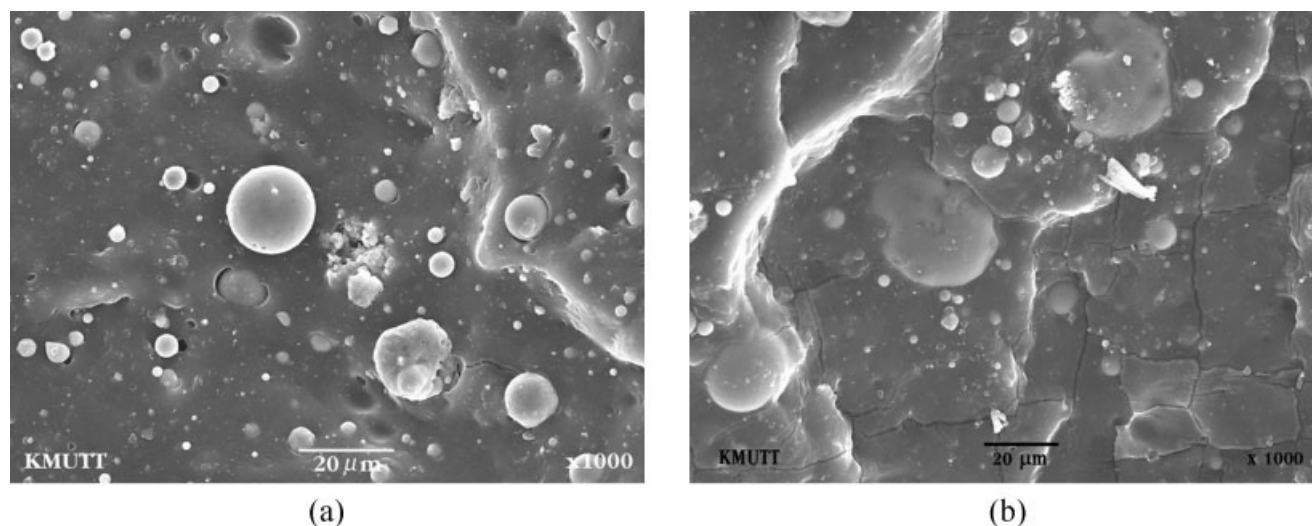
**Figure 3** Effect of FASi content on crosslink density using different Si69 concentrations for 50 : 50 NR/SBR vulcanizates.



**Figure 4** Effect of FASi content on tensile strength at different Si69 concentrations for 50 : 50 NR/SBR vulcanizates.

ings (30–50 phr). For the effect of Si69 treatment, it can be seen that the tensile strength increased with the addition of 2.0 wt % Si69 and then started to decrease at higher Si69 loadings. This indicates that the FASi/NR/SBR reinforcement was achieved at 2.0 wt % Si69. The mechanism of FASi/NR/SBR reinforcement by 2.0 wt % Si69 is discussed in depth in Schemes 1 and 2, while the decrease in tensile strength at high loading of Si69 (4.0 and 6.0 wt %) could be reasoned by a self-condensation reaction of Si69 which formed the mono- and polylayers of flexible polysiloxane molecules on the FA (silica) surface,<sup>16</sup> which could act as plasticizer between the FASi and NR/SBR molecules,<sup>17</sup> thus decreasing the filler–rubber interaction. The view can be substantiated via SEM micrographs for untreated [Fig. 5(a)] and 2 wt % Si69-treated [Fig. 5(b)] FASi/NR/SBR vulcanizates. It can be noticed that the Si69-treated vulcanizates exhibited a better phase-continuity and homogeneity at the filler–rubber interfaces, and the fly-ash particles embedded more in the rubber blend matrix. It was interesting to note that after thermal ageing, the tensile strength of the FASi/NR/SBR vulcanizates at low silica contents increased because of the postcuring reaction as mentioned earlier.

Figure 6 shows the effect of FASi and Si69 concentrations on the elongation percentage at break for FASi/NR/SBR vulcanizates before and after thermal ageing. The elongation at break of the vulcanizates was found to decrease with increasing FASi and Si69 contents, the effect being more pronounced at higher FASi and Si69 loadings. This was expected since the

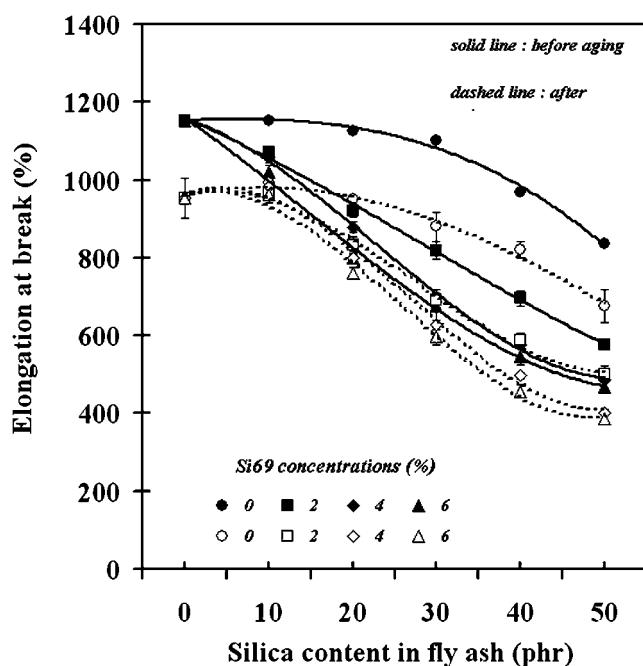


**Figure 5** SEM fracture surfaces of FASi filled NR/SBR vulcanizates (a) without Si69 (untreated) (b) with 2 wt % Si69.

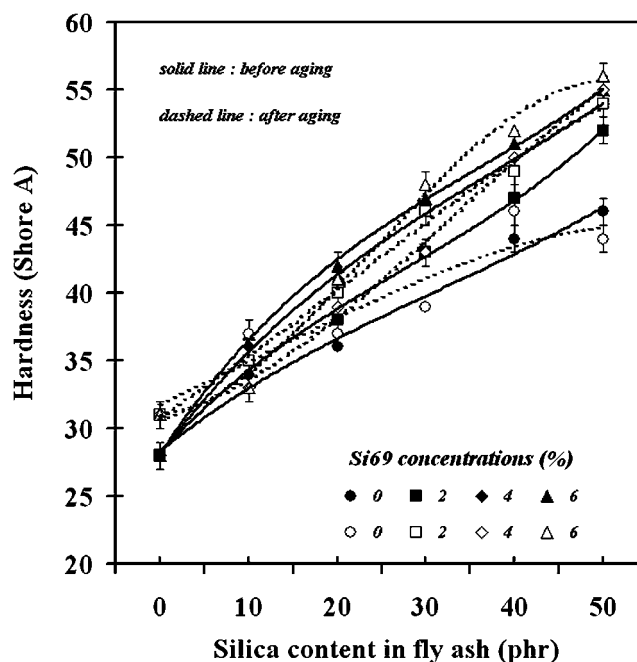
vulcanizates became more rigid (resistance to higher stress at lower elongation) as a result of C—S linkages by the presence of Si69 in the FASi/NR/SBR, as shown in Schemes 1 and 2. This statement was backed up by the hardness results as illustrated in Figure 7. It was found that the hardness of the FASi/NR/SBR vulcanizates increased with FASi and Si69 concentrations, and thermal ageing had no significant effect on the hardness.

The tear strength results of the FASi/NR/SBR vulcanizates are illustrated in Figure 8. It was found that the tear strength for the untreated FASi/NR/SBR

vulcanizates decreased with increasing FASi content, but the reverse effect was observed for the Si69-treated vulcanizates. This was expected as changes in tear strength for polymer composites are usually discussed in terms of continuity and phase interaction between filler and rubber molecules. The increase in tear strength for the treated FASi/NR/SBR vulcanizates was due to the chemical coupling reactions proposed in Schemes 1 and 2. It was also observed that the increase in tear strength was extremely considerable at 2.0 wt % Si69. At higher Si69 contents (4.0 and 6.0 wt %), the increase in tear strength became



**Figure 6** Changes in elongation at break as a function of silica and Si69 contents for 50 : 50 NR/SBR vulcanizates.



**Figure 7** Influence of FASi content in fly-ash on hardness at different Si69 concentrations for 50 : 50 NR/SBR vulcanizates.

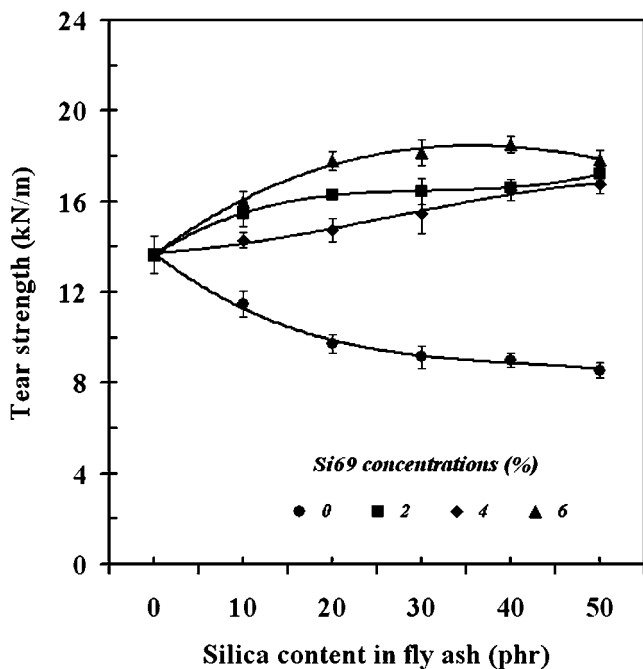


Figure 8 Effect of FASi content in fly-ash on tear strength using different Si69 concentrations for 50 : 50 NR/SBR vulcanizates.

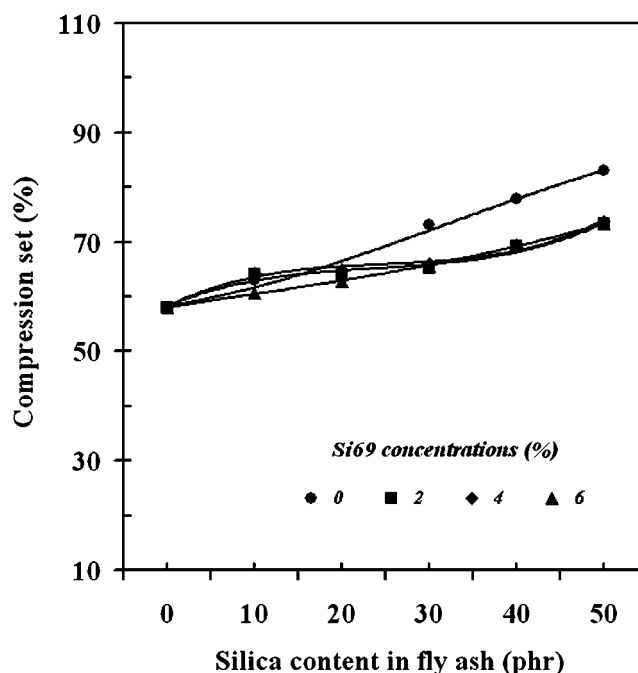


Figure 9 Variation of compression set of 50 : 50 NR/SBR blend as a function of silica and Si69 contents.

minimized because of the self-condensation reaction (plasticizing effect) as stated earlier. The continuity and phase interaction between filler and rubber molecules by the presence of FASi particles with and without Si69 could be morphologically viewed and substantiated using SEM micrographs as earlier shown in Figure 5(a,b). It can be seen that the treated-FASi/NR/SBR vulcanizates with 2.0 wt % Si69 had more continuous rubber-FA interphase than the untreated-FASi/NR/SBR vulcanizates.

The ability for the NR/SBR vulcanizates to recover after being mechanically loaded was evaluated through compression set and resilience behavior, whose results are shown in Figures 9 and 10, respectively. Generally, a decrease in compression set and an increase in resilience indicate a good elastic property of the rubber. In this work, it was observed that the elasticity of the NR/SBR vulcanizates decreased with addition of FASi, and was improved by the addition of Si69 as a result of C—S linkages in the FASi/NR/SBR vulcanizates.

Table III shows the effect of FASi and Si69 contents on the abrasive resistance. The result was reported in terms of volume loss of the vulcanizates; the greater the volume loss the lower the abrasive resistance. It was clear that the abrasive resistance for FASi/NR/SBR vulcanizates increased with increasing Si69 content, the effect being more pronounced for the optimum Si69 dosage of 2.0 wt %. There was no definite trend of the change in abrasive resistance with varying FASi contents.

### Comparison of FASi and PSi fillers

In this section, the precipitated silica (PSi) and the silica in fly-ash (FASi) were used as potential fillers in the NR : SBR vulcanizates (at blend ratio of 1 : 1) and the properties were evaluated. The 2.0 wt %

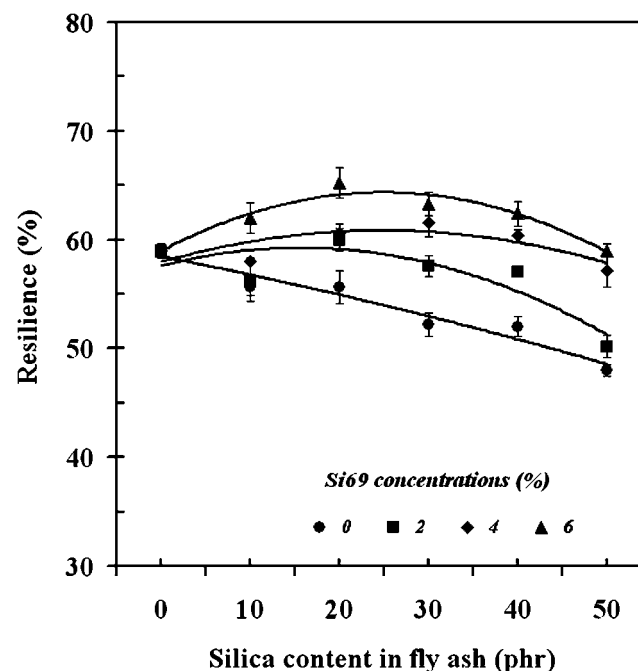


Figure 10 Effect of FASi content in fly-ash on resilience using different Si69 concentrations for 50 : 50 NR/SBR vulcanizates.



**TABLE III**  
**Effect of Silica Content on Volume Loss at Various Si69 Concentrations for 1 : 1 NR/SBR Vulcanizate**

Si69 content (%)	Volume loss (mm <sup>3</sup> ) of 1 : 1 NR/SBR vulcanizate with various FASi contents (phr)					
	0	10	20	30	40	50
0	N/A	197 ± 4	201 ± 5	178 ± 4	207 ± 5	241 ± 4
2	N/A	144 ± 1	115 ± 2	123 ± 2	131 ± 2	123 ± 1
4	N/A	132 ± 2	127 ± 1	114 ± 2	125 ± 2	125 ± 4
6	N/A	113 ± 4	116 ± 4	115 ± 2	124 ± 2	123 ± 2

Si69-treated silica contents of 20 and 30 phr were selected for this purpose. Table IV shows the cure and mechanical properties for NR/SBR vulcanizates containing 20 and 30 phr of the two silica sources. It was found that the cure time for the FASi/NR/SBR vulcanizates were lower than that of PSi/NR/SBR vulcanizates. This was because of the metal oxides in the fly-ash particles, as stated. The PSi/NR/SBR vulcanizates had better tensile properties (modulus, strength, and elongation at break) than the FASi/NR/SBR vulcanizates. The reason was associated with non-rubber content difference in these two vulcanizates. That was, for a given silica content, the amount of nonrubber content in the FASi/NR/SBR vulcanizates was greater than that in PSi/NR/SBR vulcanizates. This was because the fly-ash particles used in the FASi/NR/SBR system contained ~ 53.75% nonsilica substances, these substances diluting and replacing the rubber phase in the test specimen. However, it was interesting to note that addition of FASi filler in the NR/SBR vulcanizates exhibited better elastic properties, including compression set and resilience properties, than that of PSi filler. There were no obvious differences between these two silica sources in terms of tear strength and hardness properties.

In summary, the experimental results in this work suggested that the silica from fly-ash particles obtained from thermal power plant stations could be used effectively and satisfactorily to replace the commercial-precipitated silica in vulcanized NR/SBR blend system. Taking overall mechanical properties into account, the recommended dosage for the silica

(FASi) content was 20 phr. For more effective reinforcement, the silica from fly-ash particles had to be chemically treated with 2.0 wt % Si69 coupling agent. The use of silica from fly-ash particles proposed in this work could be beneficial for improved elastic properties of the NR/SBR vulcanizates.

## CONCLUSIONS

The experimental results suggested that the NR/SBR blend ratio at 1 : 1 (or 50 : 50 phr) gave the optimum mechanical properties for fly-ash-filled NR/SBR composites. The cure time for FASi/NR/SBR vulcanizates decreased with increasing FASi content, but increased with Si69. All mechanical properties, except the hardness, for NR/SBR vulcanizates decreased with increasing untreated FASi content. The Si69 at the recommended dosage of 2 wt % could act as an additional crosslinker in the NR/SBR vulcanizates and this resulted in improvement of the mechanical properties. The optimum tensile strength of the FASi/NR/SBR vulcanizates was achieved at 10–20 phr silica contents from fly-ash particles. Most mechanical properties were improved by thermal ageing. The overall experimental results recommended that addition of 20 phr silica from fly-ash particles treated with 2.0 wt % Si69 to the NR/SBR vulcanizates gave optimum mechanical properties and can be used to replace the commercial silica.

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**TABLE IV**  
**Property Comparison of 50 : 50 NR/SBR Compound Filled with Silica (from Fly Ash) and Commercial Silica Treated with 2% Si69**

Vulcanizate properties	Silica content of 20 phr		Silica content of 30 phr	
	FASi	PSi	FASi	PSi
Cure time (min)	16	21	14	19
Tensile modulus at 200% ( $\times 10^5$ Pa)	6 ± 1	11 ± 1	7 ± 1	12 ± 1
Tensile strength (MPa)	7 ± 1	11 ± 1	6 ± 1	14 ± 1
Elongation at break (%)	920 ± 16	1084 ± 20	819 ± 22	1124 ± 22
Tear strength (kN/m)	16 ± 0	15 ± 1	16 ± 1	18 ± 1
Hardness (Shore A)	38 ± 1	38 ± 1	43 ± 1	43 ± 1
Compression set (%)	64 ± 1	71 ± 0	65 ± 1	76 ± 1
Resilience (%)	60 ± 1	37 ± 0	58 ± 1	31 ± 0
Abrasion (mm <sup>3</sup> )	115 ± 2	126 ± 2	123 ± 2	111 ± 1

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